# Styrenation of Allylsucrose Improves Its Properties As a Coating Material

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The preparation and properties of allylsucrose (1) have been described in publications from this Laboratory. It has been shown that allylsucrose containing from six to seven allyl groups undergoes oxidative polymerization characteristic of drying oils, producing coatings with high gloss, hardness and good resistance to solvents, oils and heat. Since blown allylsucrose dissolves in a variety of solvents to give solutions of low viscosity and high solids content and produces resistant films of fast set time, it may have diverse applications in the coating industry. In addition to its primary use as a coating material, allylsucrose recently has been suggested as an upgrader for drying oils (2). The copolymerization of allylsucrose with drying oils (2) and unsaturated esters (1-c) has now been extended to styrene, a monomer that has already attracted considerable attention as a component of styrenated drying oils (3).

At present allylsucrose is most suitable in applications where resistance to organic solvents, heat and abrasion are the prime considerations; modified formulations are required to impart improved water resistance. Methods proposed for achieving this end include the following: (a) preparation of derivatives by substitution of ether or ester groups for free hydroxyls, (b) addition of hydrophobic resins or plasticizers, and (c) copolymerization with any unsaturated organic compound capable of forming chain polymers through its double bond.

Methods (a) and (b) have been tried, with promising results (4). Copolymerization with styrene was initiated because of the low cost of this monomer and the clarity, water resistance, lack of color, and toughness of polymeric styrene. Early work on the copolymerization of styrene with drying oils has been described in the patent literature. In 1946, however, Hewitt and Armitage (5) offered a theoretical interpretation of the styrenation reaction and disclosed methods for polymerizing styrene with drying oils in the presence of inert solvents. Later the Dow Chemical Co. (6) summarized the emulsion, solvent and mass methods for the styrenation of drying oils and introduced the use of $a$-methylstyrene in conducting practical mass polymerizations leading to homogeneous products. The characteristics of some styrenated raw and oxidized drying oils, prepared according to the suggested recipes in this publication, have been reported recently by Schroeder and Terrill (7-a); and by Hoogsteen, Young and Smith (7-b). In our work the variables studied in somewhat similar procedures were: (a) ratio of total styrenes to allylsucrose, (b) ratio of styrene to

α-methylstyrene, (c) type of catalyst, (d) concentration of the catalyst and (e) peroxide number of blown allylsucrose. The products were examined for color, viscosity and clarity. Curing times were established by curing test panels at 100 or 150° C., and solvent resistance tests were carried out with coated test tubes air-dried or cured in an oven for the proper time.

### Styrenation of Raw (Unblown) Allylsucrose

Preliminary experiments were carried out by heating allylsucrose and various proportions of styrene in the presence of 0.25-1 per cent of benzoyl peroxide or cumene hydroperoxide at 80-170° for 25 to 110 minutes. When the original monomer mixture contained 33 to 66 per cent of styrene, varnishes of superior resistance were obtained. In most cases, the films, however, were hazy. Since the haziness was probably due to the formation of high molecular weight polystyrene incompatible with allylsucrose, moderators such as α-methylstyrene and diallylether were added. Although varnishes of good resistance were again obtained, these agents did not completely eliminate the haziness. The Dow procedure for the styrenation of raw drying oils (6) was then adopted with modifications. Styrene containing 30 per cent of α-methylstyrene and catalytic quantities of benzoyl peroxide was added gradually to allylsucrose at 140° C. By this slow addition technique, however, it was not possible to add more than 13 per cent of styrene before gelation occurred. Products that contained five to 10 per cent of polymerized styrene exhibited poor cohesive properties. In view of the cloudiness of most of the films and the low conversion of styrenes which characterized the products from unblown allylsucrose, the styrenation of blown allylsucrose was then investigated.

### Styrenation of Blown Allylsucrose

Table I briefly summarizes the various recipes employed and gives the quantities of monomeric styrenes at the end of the reaction; Table II records the Sward hardness and the results of resistance tests of baked and air-dried films prepared from the best products decribed in Table I. The successful recipe utilizing a-methylstyrene along with styrene for the styrenation of oxidized drying oils (6) was the starting point for all our experiments. As a result of many runs in which the peroxide number of blown allylsucrose ranged from 26 to 236, it was found that a value of 50-60 gave the highest conversion of styrene prior to gelation. Conversion without catalyst was unsatisfactory (Expt. 1), but addition of various peroxide catalysts (Expts. 2-8) brought about good conversion and produced varnishes of good resistance. These experiments indicate that moderate variation in the quantity of added peroxide as well as the peroxide number is possible. The recipes marked with superscript (a) were the most successful from the point of view of reduced reaction time, low volatiles and quality of films. Variation in these recipes by altering the proportions of styrene to α-methylstyrene (Expts. 9 and 10), the total styrenes (Expts. 11 and 12) and the peroxide number of blown allylsucrose (Expts. 13 and 14) gave adequate conversion of styrene but films of inferior resistance.

Table I. Styrenation of Blown Allylsucrose at 125° C.

| Expt. No. | Peroxide Number of Allyl-sucrose | Total Styrenes, per cent | Ratio of styrene to alpha-methyl-styrene | Catalyst, per cent (Based on total monomers) | Reaction Time, hrs. | Corrected Volatiles, per cent | Solubility in toluene |
|---|---|---|---|---|---|---|---|
| 1 | 55 | 50 | 70:30 | none | 18 | 11.3 | Sol. |
| 2 | " | " | " | 0.5 per cent Bz$_2$O$_2$ | 11.1 | 8.1 | " |
| 3a | " | " | " | 0.5 per cent t-butyl hydroperoxide | 3.8 | 5.5 | " |
| 4a | " | " | " | 0.65 per cent cumene hydroperoxide | 9.5 | 5.3 | " |
| 5 | 56 | " | " | 0.5 per cent Uniperox 60 | 9.5 | 6.5 | " |
| 6a | 52 | " | " | 1 " " " | 7.2 | 5.5 | " |
| 7 | 62 | " | " | 2 " " " | 3.8 | 3.3 | " |
| 8a | 62 | " | " | 0.75 " " " | 5.7 | 7.5 | " |
| 9 | 54.5 | " | 60:40 | 0.65 per cent cumene hydroperoxide | 12.5 | 7.3 | " |
| 10 | " | " | 80:20 | " " " " | 2.2 | 3.5 | Ins. |
| 11 | " | 40 | 70:30 | " " " " | 7.3 | 5.2 | Sol. |
| 12 | 59.4 | 60 | " | " " " " | 7.0 | 4.1 | " |
| 13 | 25.7 | 50 | " | " " " " | 7.0 | 5.6 | " |
| 14 | 101.3 | " | " | " " " " | 6.0 | 8.8 | " |

a Recommended recipe.

Table II. Evaluation of Styrenated Allylsucrose

| Expt. No. | Curing Time, hrs. at 100° C. | Sward Hardness | 50 per cent Ethanol | 4 per cent Acetic Acid | 5 per cent Sodium Hydroxide | Acetone | Distilled Water | Boiling Water | Clarity of Films |
|---|---|---|---|---|---|---|---|---|---|
| | | | | ←————Resistance time in hours a————→ | | | | | |
| 3 | 2 | 62 | >72 | >72 | 48 | 1 | >72 | >12 | Clear |
| 4 | 2 | 64 | >72 | >72 | 3 | >72 | >72 | >12 | Clear |
| 6 | 2 | 62 | >72 | >72 | 3 | >72 | >72 | >12 | Clear |
| 8 | 3 | 60 | >72 | >72 | 48 | 6 | >72 | >12 | Clear |
| Control (Blown Allyl-sucrose) | 2 | 62 | 3 | 5 | 10 min. | 15 | 48 | 1 min. | Clear |
| Air Drying 6 | b | 62 | >72 | 6 | 3 min. | >72 | 72 | >12 | Clear |

a The films were examined at 10-minute intervals for the first hour, hourly for seven hours, then at 24, 48 and 72 hours. The times recorded are those when failure was noted. Tests were discontinued at 72 hours generally and at 12 hours in the case of boiling water.
b Dried to touch at room temperature in 0.5 hr.; dried hard in four hrs. Resistance tests carried out after curing for two weeks at room temperature.

*Figure* 1 shows that the production of polymer in the styrenation of blown allylsucrose followed much the same course reported for styrene-drying oil copolymers. Although the amount of free styrene was reduced fairly rapidly, attempts to reach more complete conversion were nullified by formation of intractable gels. Careful termination of the reaction when the first signs of gel appeared was necessary to insure formation of products soluble in a suitable varnish thinner.
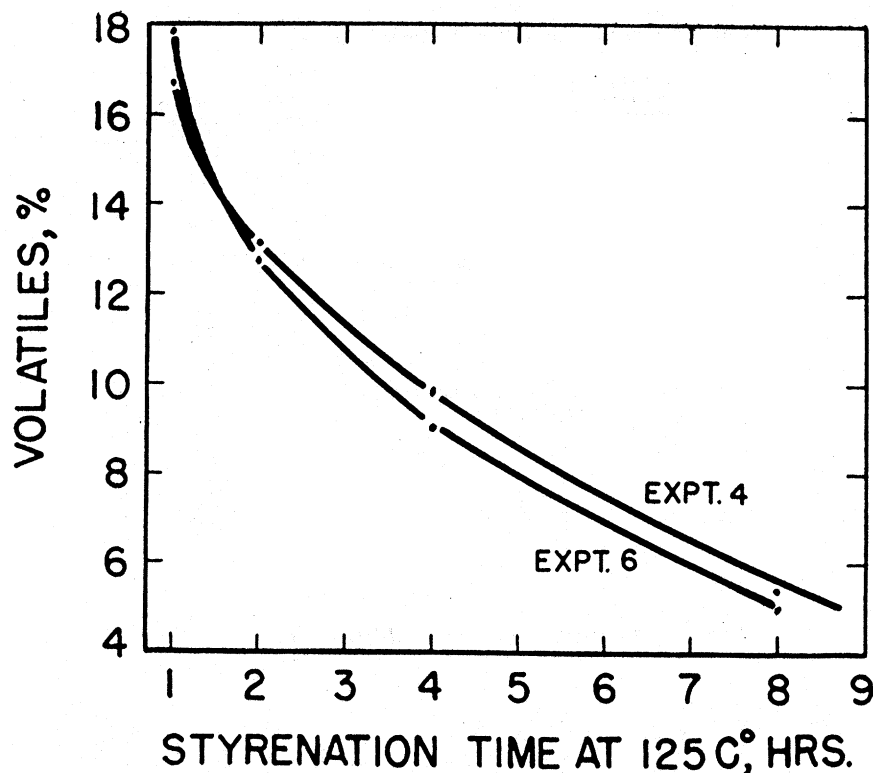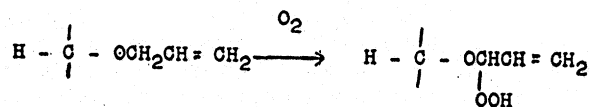
*Fig. 1—Styrenation of Blown Allylsucrose: Unconverted Styrenes as a Function of Time*
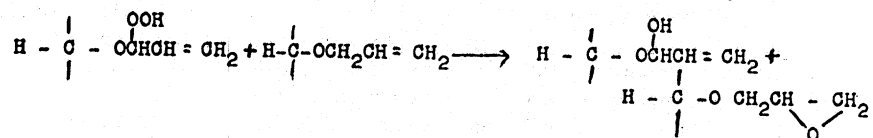
In addition to the baked films cured at 100° listed in *Table II*, films cured at 150° G. and by air-drying were also studied. In the last-mentioned case, test tubes were coated with toluene solutions of styrenated allylsucrose containing 0.1 per cent cobalt as cobalt octoate. After the films were cured at room temperature for two weeks, the solvent resistance was determined. The air-dried films as well as those cured at 150° C. showed excellent resistance to boiling water, but were less resistant to some of the other test solutions than films of the same varnishes cured at 100° C. An examination of *Table II* reveals the superior solvent resistance of styrenated blown allylsucrose over blown allylsucrose itself.

### Discussion

In blowing allylsucrose, the peroxide number can be attributed to the participation of allyl groups in the formation of the following structure (1-a):

$$H - \overset{|}{\underset{|}{C}} - OCH_2CH = CH_2 \xrightarrow{O_2} H - \overset{|}{\underset{|}{C}} - OCHCH = CH_2$$
$$\underset{OOH}{|}$$

Inasmuch as in the styrenation of oxidized drying oils the peroxide content of the oil seems to catalyze the styrenation, it might be assumed that a similar mechanism could be followed with blown allylsucrose. Actually, after prolonged heating of styrene and blown allylsucrose with a peroxide number of 100 or more at 125° C., poor conversion of styrene and gelation of the mixture resulted when this technique was employed. The hydroperoxide may react with neighboring allyl groups preferentially as follows

$$
H - \overset{|}{\underset{|}{C}} - O\overset{OOH}{\underset{}{C}}HCH = CH_2 + H-\overset{|}{\underset{|}{C}}-OCH_2CH = CH_2 \longrightarrow H - \overset{|}{\underset{|}{C}} - O\overset{OH}{\underset{}{C}}HCH = CH_2 +
$$

$$
H - \overset{|}{\underset{|}{C}} -O\ CH_2CH - CH_2
$$

rather than initiate the formation of styrene chains. When 0.5 per cent of benzoyl peroxide, or t-butyl hydroperoxide or 0.65 per cent cumene hydroperoxide was added to a blown allylsucrose-styrene mixture, more styrene was converted to polymer or copolymer within a shorter time. The benzoyl peroxide, however, gave products which had poorer solvent resistance. A partial explanation may be the fact that the more rapid decomposition of the benzoyl peroxide at 125° liberates radicals so quickly that shorter polystyrene chains are formed. The formation of shorter polystyrene chains may also explain the longer curing time (three hours) required for Expt. 2 (*Table I*). The slower decomposition of t-butyl hydroperoxide (8) may be considered as roughly equivalent to the gradual addition of benzoyl peroxide throughout the reaction.

In an attempt to gain proof of the copolymerization of styrene and allylsucrose, an experiment was adapted from D'Alelio (9). First a mixture of styrene and α-methylstyrene was polymerized in the presence of benzoyl peroxide under the same conditions as the styrenation. The molecular weight of the polystyrene formed was 11,500 when measured in toluene viscosimetrically. Mixtures of blown allylsucrose and this polystyrene were compared with the supposed copolymer. The differences in the solubility of copolymer and the mixture in cyclohexane suggested that a certain amount of true copolymerization took place. The labile hydrogen atom of the allyl group, at the seat of peroxide formation, and the consequent allylsucrose radical may function as chain transfer agents similar to unconjugated drying oils. Styrenated blown allylsucrose appears to be a mixture of true copolymer, polystyrene and polymeric allylsucrose.

Attempts to modify the tendency to gelation by the addition of carbon tetrachloride, dehydrated castor oil and amyl mercaptan as chain-transfer agents were not encouraging. Carbon tetrachloride gave discolored products, dehydrated castor oil prolonged the reaction time excessively, and the mercaptan gave products with inferior resistance.

### Experimental

*Starting Materials*: Styrene and α-methylstyrene were kindly supplied by the Dow Chemical Co.* These materials were washed with 10 per cent sodium hydroxide, then with distilled water. The organic layers were finally separated, and dried over anhydrous calcium sulfate before use. Unblown

allylsucrose was prepared from sucrose and allyl chloride in a stainless steel (316) autoclave. This material approximated the product prepared in a glass-lined autoclave (1-c) ; allyl (Wijs) 5.8; hydroxyl 1.7; $n_D^{25°}$ =1.4890.

Blown allylsucrose was prepared by passing oxygen through 250-g. portions of allylsucrose in a 500-cc. three-neck flash immersed in a bath maintained at 80° C. Bubbles of oxygen were introduced through a 2-mm. capillary inlet tube attached to a 24/40 standard taper joint. The oxygen was introduced at a rate of 7.5 liters per hour at the bottom of the flask and was distributed through the liquid by a glass half-moon stirrer rotating at 408-410 revolutions per minute. The third neck of the flask was connected to a flowmeter to control the flow of oxygen. It was possible to obtain reproducibly blown oil by determining the peroxide number periodically by a modified Wheeler method (10). In our determinations, the reaction mixtures were allowed to stand for 15 minutes, rather than one minute, before titration. The peroxide catalysts were assayed in the same manner:

<p align="center"><em>Table III. Blowing Allylsucrose at 80° C.</em></p>

| Hours | Peroxide Number[a] | $n_D^{25°}$ | Viscosity, stokes |
|---|---|---|---|
| 0 | 5 | 1.4890 | 5 |
| 2 | 112 | 1.4910 | 11 |
| 4 | 236 | 1.4954 | 148 |
| 6 | 245 | 1.4997 | "molasses" |

*Styrenation*: (a) Unblown allylsucrose: Styrene containing $a$-methylstyrene (30 per cent) and a peroxide (1.35 per cent) was added slowly to allylsucrose at 140° C. Reaction was continued until the mixture was close to gelation.

(b) Blown allylsucrose: All the ingredients were loaded into three-neck, 500-cc. reaction flasks at the beginning of the reaction. The flasks were then immersed in thermostatically controlled oil baths maintained at 125° throughout the reaction. The reaction flasks were swept out with nitrogen of high purity before the start of the reaction, and this atmosphere was maintained during the reaction. Mechanically driven glass stirrers were used in reactions. When the reaction mixture was about to gel, toluene was added, and the mixture was stirred until solution occurred.

*Determination of Volatiles*: As the styrenation proceeded, 2-g. samples were removed at various intervals. These samples plus 0.2 per cent hydroquinone were heated in an oven at 135° C. until constant weight was attained (usually 10 hours). Controls were run on allylsucrose and hydroquinone, and a correction was made for loss of volatile material by allylsucrose.

*Evaluation of Films*: Toluene solutions of styrenated allylsucrose were made up to a viscosity of 150 centistokes. Films poured on glass panels were heated at 100 or 150° C. until cured, as determined by the fingernail test.

Test tubes (6 x ⅝ inch) dipped in a solution contained in a 27-mm. wide graduate were withdrawn mechanically at a rate of two inches per

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a Peroxide number=number of millimoles of peroxide in 1000 g. of an oil.

minute. After the films were cured the test tubes were suspended in beakers containing the test solutions.

Undercure gave films with poor resistance; long cures gave films with improved resistance to acetone and alkali without impaired resistance to other solutions.

## Acknowledgment

## Summary

Allylsucrose can be styrenated by a simple mass method to give homogeneous products which form clear films with improved water and alkali resistance. High conversion of styrene can be attained in a relatively short reaction time by employing (a) blown allylsucrose of peroxide number 50-60; (b) 50 per cent styrene (70 per cent styrene: 30 per cent a-methylstyrene); (c) 0.5 to 0.65 per cent peroxide catalyst (t-butyl or cumene hydroperoxides rather than benzoyl peroxide), and (d) a reaction temperature of 125° C.

Films air-dried or baked at 150° C. had excellent resistance to boiling water, but films cured for 1 hour at 100° C. had superior over-all solvent resistance.

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